

To Cite:

Parthasarathy V, Sundaresan B, Dhanalakshmi V, Anbarasan R.
Free radical grafting of ethylcrotonate and ethylsalicylate onto
HDPE by thermolysis method - an FTIR approach. *Discovery*, 2022,
58(322), 1045-1053

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Peer-Review History

Received: 27 July 2022

Reviewed & Revised: 29/July/2022 to 02/September/2022

Accepted: 05 September 2022

Published: October 2022

Peer-Review Model

External peer-review was done through double-blind method.



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DISCOVERY
SCIENTIFIC SOCIETY

Free radical grafting of ethylcrotonate and ethylsalicylate onto HDPE by thermolysis method - an FTIR approach

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Anbarasan R^{3*}

ABSTRACT

High Density Polyethylene (HDPE) was functionalised with two different esters in an inert atmosphere of 160⁰ C under different experimental conditions by thermolysis method. Ester functionalised HDPE was characterized by FTIR, DSC and TGA analytical tools. The order of functionalization, C=C formation and crosslinking reactions were determined by FTIR based kinetic method.

Keywords: HDPE; Functionalization; Esters; FTIR; DSC; TGA; Kinetics.

Abbreviations: HDPE-High Density Polyethylene; DCP-Dicumyl peroxide; DSC-Differential Scanning; Calorimetry; TGA-Thermo Gravimetric Analysis; FTIR-Fourier Transform Infrared; EC-Ethylcrotonate; ES-Ethylsalicylate; PE-Polyethylene.

1. INTRODUCTION

Polyolefin is a polymer produced from a simple olefin (also called an alkene) as a monomer. The term polyolefin typically is applied to polymers derived from ethylene, propylene, isobutylene, cyclic olefins, and butadiene, and other alpha-olefins and diolefins. Polymers are essential materials for almost every industry as adhesives, building materials, paper, cloths, fibers, coatings, plastics, ceramics, concretes, liquid crystals, photoresists and coatings. They are also major components in soil and plant and animal life. They are important in nutrition, engineering, biology, medicine, computers, space exploration, health and environment. Even though it has numerous applications, its non bio-degradable property results in polluting the environment throughout the world. So inevitably, it was banned in many countries. Researchers from various R&D sectors have been involved in developing bio-degradable polyolefins for the past four decades. Among the polyolefins, polyethylene (PE) has a great speciality due to its excellent manufacturing property and processability. These properties are

enhanced by surface modification process i.e. introduction of a functional group onto the backbone of PE for environmental green polymer. Melt functionalization of PP with allyl co-agents in the presence of a free radical was carried out (Sengupta & Mclean, 2005). PP was aminated by melt functionalization method and the resultant product was characterized by FTIR, NMR and rheological and mechanical tests (Lu & Horrión, 2005). Fallani et al. (2003) studied the photo initiated surface modification of LDPE. The thermal decomposition of dialkyl peroxides, peroxy ketals and peroxy ester was reported by Maillard and co-workers (2000). The results on chemical modification of PP by thermolysis of peroxy ketals were reported by Saule and his research team (Navarre et al., 2001; Saule et al., 2003). Isotactic PP was functionalized with maleic anhydride by reactive extrusion method in the presence of NdO (Zhu et al., 2006). Parameters affecting the functionalization of LLDPE in an internal mixer were clearly understood from Agñeh and his research team (Aghñeh et al., 2006). Unsaturated peroxides were used for the chemical modification of PP (Saule et al., 2005). Glycidyl methacrylate was grafted onto iPP by Benzoyl peroxide initiation method (Brahmbhatt et al., 2001). In the present investigation, functionalization of HDPE with Ethylcrotonate and Ethylsalicylate, in the presence of dicumyl peroxide (DCP), as a free radical initiator is reported. The novelty of the present investigation is in reporting the FTIR based kinetics for crosslinking, C=C formation and functionalization process under different experimental conditions.

2. MATERIALS AND METHODS

High density polyethylene (HDPE) was purchased from Ottokemi, India. In order to remove the antioxidant present in the HDPE sample, it was purified prior to thermolysis reaction. The purification procedure was explained in our previous publication (Anbarasan et al., 2005). Dicumyl peroxide (DCP, Ottokemi, India), 1,2-dichloro benzene (AR, Loba Chemi, India), Ethylcrotonate (EC, Lancaster, UK) and Ethylsalicylate (ES, Ottokemi, India), Dichloromethane (AR, Merck, India), Acetone (AR, Paxmy, India) and Toluene (Loba Chemi, India) used for further experimentation were used without subjecting them to any process. FTIR spectra of HDPE samples in the form of film before and after peroxide treatment were recorded, using Shimadzu 8400 S FTIR spectrophotometer instrument. In FTIR film preparation, the soluble part of the modified HDPE alone was considered. Then the spectrum was recorded. The baseline correction was made carefully and the area of the peaks was determined using FTIR software. For the quantitative determination of percentage grafting, the area of the peaks at 1730 and 720 cm^{-1} was determined and relative intensity was calculated as follows:

$$\text{Relative intensity carbonyl (RI)} = A_{1730}/A_{720}$$

$$\text{Relative intensity of C=C (RI)} = A_{1604}/A_{720}$$

$$\text{Percentage Ester grafting} = \frac{\text{RI}_{\text{ester}} \times W}{C \times 1.52} \times 100 \quad \text{----- (1)}$$

$$\text{Percentage C=C formation} = \frac{\text{RI}_{[\text{C}=\text{C}/\text{C-H}]} \times W}{C \times 0.35} \times 100 \quad \text{----- (2)}$$

where, W is the weight of non-cross linked polymer, C is the % weight of peroxide and 1.52 is the calibration coefficient, as mentioned in our earlier publication (Anbarasan et al., 2005). DSC was recorded for the samples by using SDT 2960 simultaneous TGA and DSC, TA instruments under Nitrogen atmosphere at the heating rate of 10° C/min. The TGA analysis was performed under air purge at the heating rate of 10° C/min by using the SDT 2960 simultaneous TGA and DSC, TA instruments. The % crosslinking was determined by using the following formula:

$$\% \text{crosslinking} = \frac{[\text{Weight of Polymer taken for functionalization}] - [\text{Weight of Non-cross linked polymer obtained after functionalization}]}{\text{Weight of Polymer taken for functionalization}} \times 100 \quad \text{----- (3)}$$

3. RESULTS AND DISCUSSION

In the functionalization of HDPE, two types of esters such as EC and ES were used. Equal % weight of DCP and esters were used. Functionalization reaction was carried out under different experimental conditions like variation in (% weight of DCP), temperature and reaction time.

3.1. FTIR Characterization

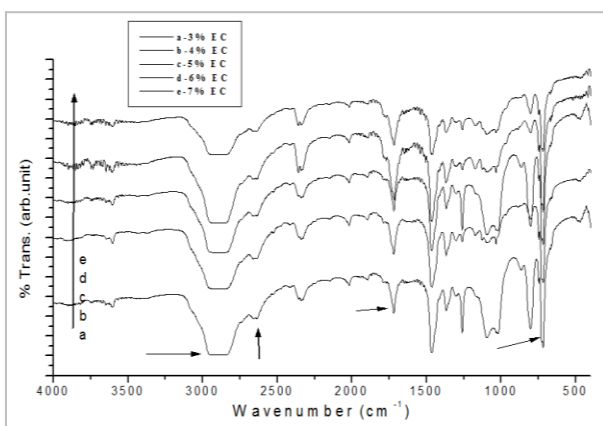
The FTIR spectra of functionalized HDPE with different % weight of EC are shown in Fig.1. Important peaks are summarized below: Peaks between 2600 and 3000 cm^{-1} were associated with the C-H stretching vibrations. The stretching of -C=O- bond could be seen at 1723 cm^{-1} . The C-H bending vibration was observed at 1490 cm^{-1} . A sharp peak at 730 cm^{-1} corresponded to the C-H deformations. The new peak which appeared at the wave number of 1050 cm^{-1} was used to confirm the C-O-C ester linkage. A peak at 1610 cm^{-1} confirmed the formation of olefin linkage (C=C) after melt functionalization reaction. The other peaks correspond to pure HDPE. Fig.2 illustrates the FTIR spectra of ES functionalized HDPE under different % weight of ES. Here also, the above mentioned peaks were observed. The FTIR spectra of EC and ES functionalized HDPE under different temperature and time interval was not shown here.

3.2. Effect of % weight of DCP on % functionalization, % crosslinking and C=C formation

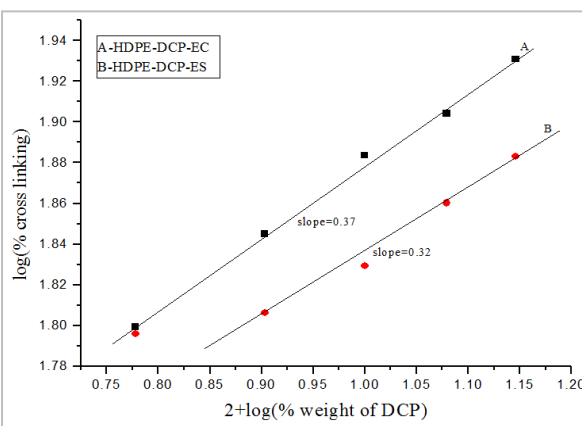
The % weight of DCP and EC were used in equal concentrations. In the present investigation, the % weight of EC varied between 3 and 7. While increasing the (% weight of DCP), the % ester grafting was also increased. This may be due to the availability of more free radicals, derived from DCP, for grafting of EC onto HDPE. In order to find out the order of the functionalization reaction, a log-log plot was made between log (% weight of DCP) and log ($\text{RI}_{[\text{C=O/C-H}]}$). Fig.3A represents the same with a straight line. The relative intensity increases with increase in the (% weight of DCP). The slope value was determined as 1.5, which confirmed the 1.5 order of functionalization reaction with respect to (% weight of DCP). The same type of plot was made for ES system also (Fig.3B). The slope value was determined as 1.25. This confirmed the 1.25 order of functionalization reaction with respect to (% weight of DCP). The rate of functionalization (R_f) can be written as follows: $R_f \propto (\% \text{ weight of DCP})^{1.5}$ for EC and $R_f \propto (\% \text{ weight of DCP})^{1.25}$ for ES grafted HDPE. It means that 1.5 mol of DCP is required to functionalize 1 mol of HDPE for EC and 1.25 mole of DCP is required to functionalize 1 mol of HDPE for ES systems. During the functionalization reaction, both crosslinking and C=C formation (peak which appears at 1650 cm^{-1} in FTIR spectrum) were competitive. The possible crosslinking reaction was analyzed kinetically. For this, the plot was made between log (% weight of DCP) and log (% crosslinking) as shown in Fig.4A. The slope value was determined as 0.37 which confirmed 0.50 order of crosslinking reaction with respect to (% weight of DCP). For ES system, the slope was found to be 0.32 (Fig.4B). This confirmed the 0.50 order of crosslinking with respect to (% weight of DCP). The rate of crosslinking (R_{CL}) reaction can be written as follows: $R_{CL} \propto (\% \text{ weight of DCP})^{0.50}$ for both EC and ES systems. It means that 0.50 mol of DCP is required to crosslink 1 mol of HDPE for both EC and ES grafted systems. The oxidative degradation reaction lead to C=C formation during the melt functionalization reaction. This was analyzed by the universal log-log plot method. The plot was made between (% weight of DCP) and log ($\text{RI}_{[\text{C=C/C-H}]}$) (Fig.5A) and the slope value was determined as 1.2, which confirmed the 1.25 order of C=C formation reaction with respect to (% weight of DCP) for EC grafted system. Similar type of plot was made for ES (Fig.5B) system and the slope value was found to be 1.33. This confirmed the 1.50 order of double bond formation with respect to (% weight of DCP). The rate of double bond formation (R_{DB}) can be written as follows: $R_{DB} \propto (\% \text{ weight of DCP})^{1.25}$ for EC and $R_{DB} \propto (\% \text{ weight of DCP})^{1.5}$ for ES system. It means that 1.25 mol of DCP is required to form 1 mol of olefin bond in HDPE backbone for EC and 1.5 mol of DCP is required to form 1 mol of olefin bond in HDPE backbone for ES system. Table - 1 showed % functionalization, crosslinking and C=C formation values for EC and ES grafted HDPE.

Table 1 Effect of % weight of DCP on functionalization, crosslinking and C=C formation

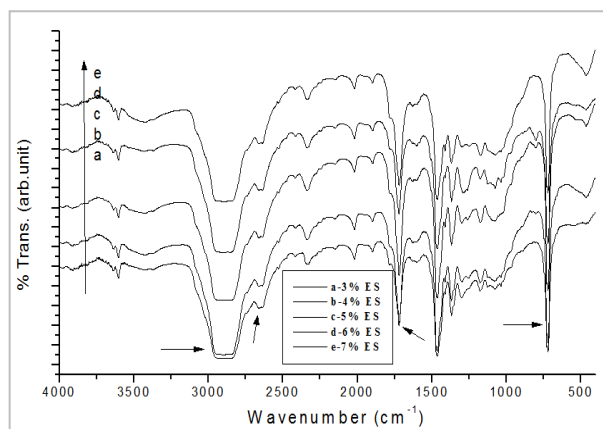
% weight of DCP	% functionalization		% cross linking		% C=C formation	
	EC	ES	EC	ES	EC	ES
3	19.21	54.29	63.0	52.5	1.14	1.20
4	22.50	62.37	70.0	56.0	3.32	1.68
5	25.34	74.76	76.5	60.5	4.45	2.43
6	40.74	79.62	80.2	64.5	5.54	2.74
7	56.93	82.96	85.3	69.5	7.24	3.97

**Figure 1**

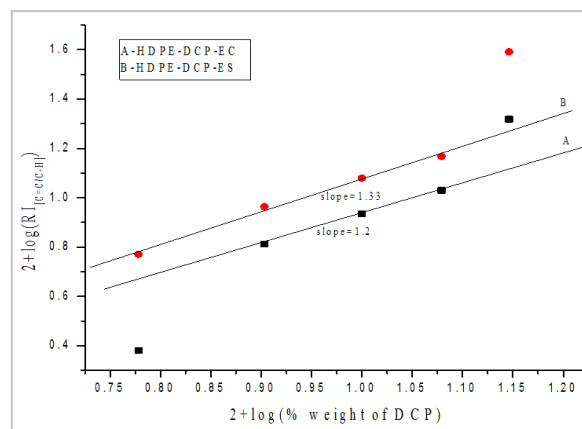
FTIR spectrum of EC functionalized HDPE under different % weight of EC-DCP

**Figure 4**

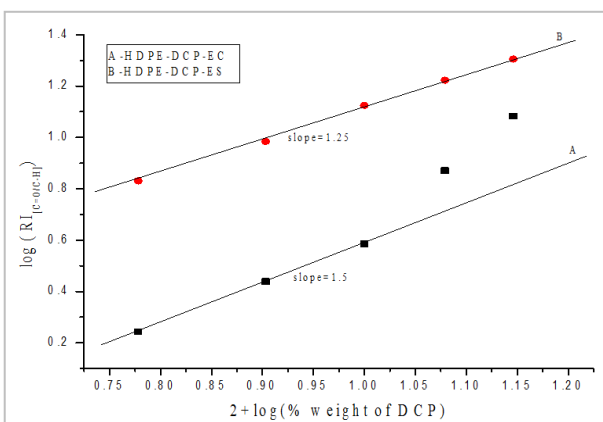
Effect of % Weight of DCP on % Cross linking (A) HDPE-EC, (B) HDPE-ES Time = 2 h, Temperature 160°C, Weight of LDPE-2.0 g

**Figure 2**

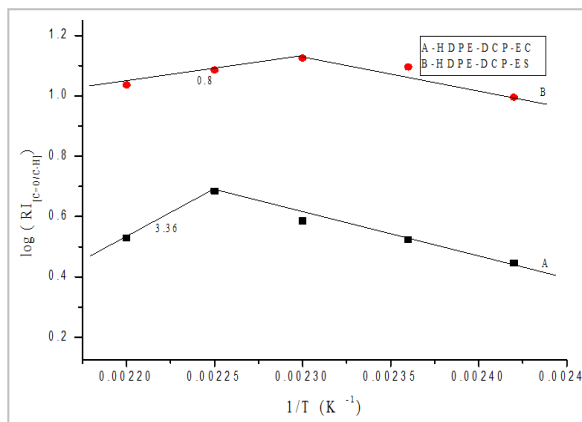
FTIR spectrum of ES functionalized HDPE under different % weight of ES-DCP

**Figure 5**

Effect of % Weight of on C=C formation (A) HDPE-EC, (B) HDPE-ES Time = 2 h, Temperature 160°C, Weight of LDPE-2.0 g

**Figure 3**

Effect of % Weight of on DCP on RI of (A) HDPE-EC, (B) HDPE-ES Time = 2 h, Temperature 160°C, Weight of LDPE-2.0 g

**Figure 6**

Effect of Temperature on functionalization (A) HDPE-EC, (B) HDPE-ES Time = 2 h, % weight of DCP-5%, Weight of LDPE-2.0 g

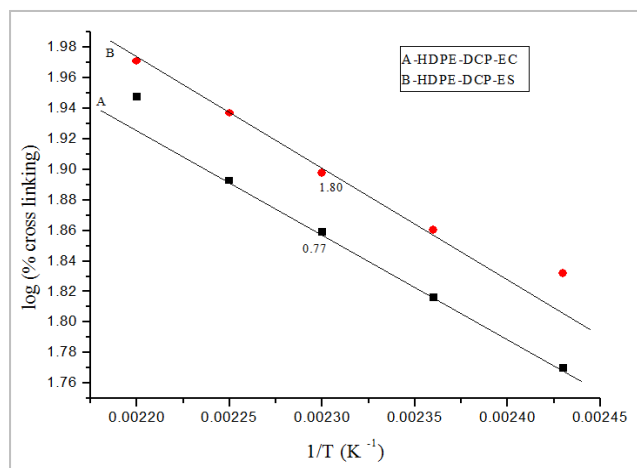


Figure 7

Effect of Temperature % cross linking of (A) HDPE-EC, (B) HDPE-ES Weight of HDPE = 2.0 g. Time = 2 h. % Weight of DCP = 5%.

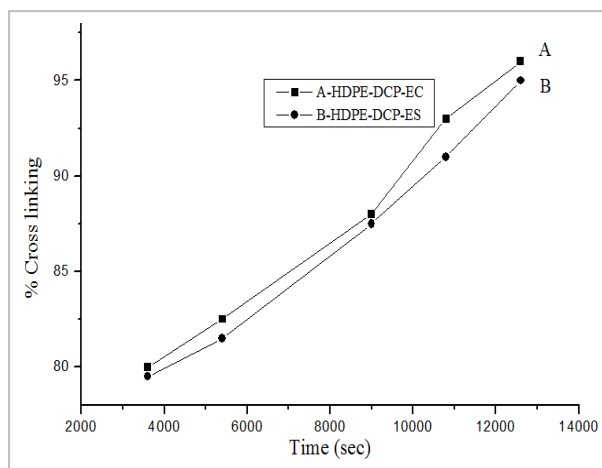


Figure 10

Effect to Time on % cross linking (A) HDPE-EC, (B) HDPE-ES Weight of HDPE = 2.0 g, Temperature = 160°C, % weight of DCP = 5%.

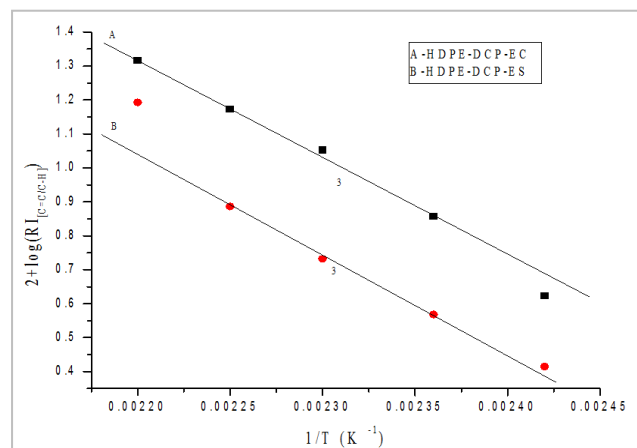


Figure 8

Effect to Temperature on C=C formation of (A) HDPE-EC, (B) HDPE-ES Time = 2 h, % weight of DCP = 5%, Weight of LDPE = 2.0 g

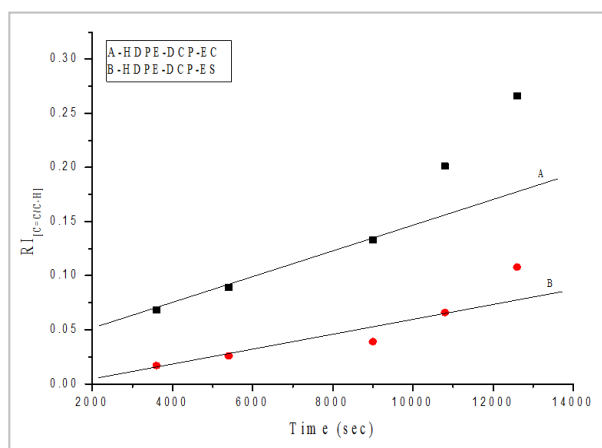


Figure 11

Effect to Time on C=C formation of (A) HDPE-EC, (B) HDPE-ES Temperature = 160°C, % weight of DCP = 5%, Weight of LDPE = 2.0 g

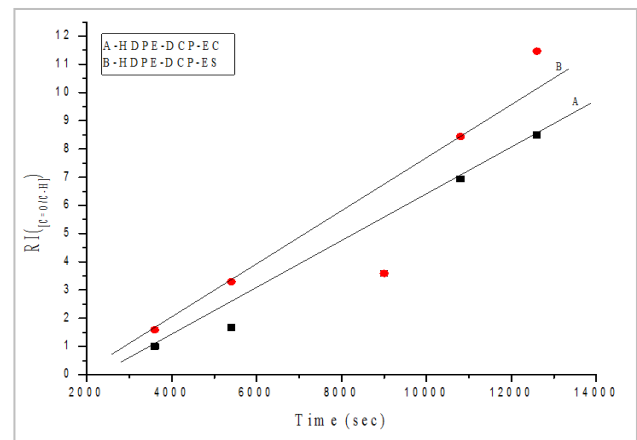


Figure 9

Effect to Time on functionalized of (A) HDPE-EC, (B) HDPE-ES Temperature = 160°C, % weight of DCP = 5%, Weight of LDPE = 2.0 g

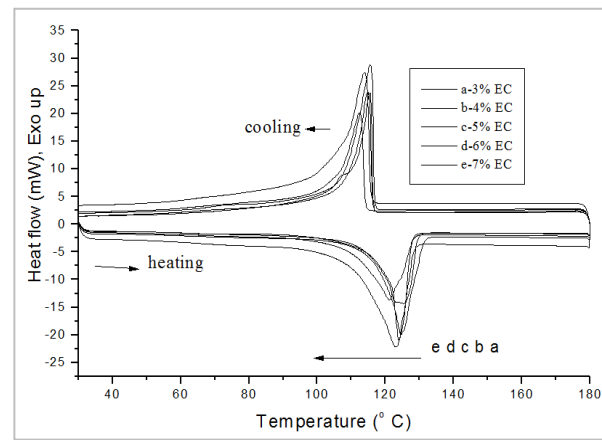


Figure 12

DSC of ES functionalized HDPE at different % weight of ES

3.3. Effect of temperature on % functionalization, % crosslinking and C=C double bond formation

While increasing the temperature, % ester grafting was increased up to 160°C then it was decreased. This is due to the formation of unwanted by-products at higher temperature, with very high activation energy. The activation energy (E_a) for the functionalization of EC onto HDPE was determined from the Arrhenius plot i.e. plot of $1/T$ Vs $\log(RI_{[C=O/C-H]})$ (Fig.6A). The slope was determined and the E_a value was calculated as 236 kJ/mol. The E_a for the functionalization of ES onto HDPE was determined as 196 kJ/mol (Fig.6B). This inferred that EC consumes more amount of heat energy for functionalization rather than ES. The lower E_a value supported the higher % grafting of ES onto HDPE backbone. The % grafting values are given in the Table - 2. The role of temperature on crosslinking reaction was also analyzed. Fig.7A indicates the plot between $1/T$ and $\log(\% \text{ crosslinking})$ for EC system with the E_a value of 167 kJ/mol. The same plot was made for ES (Fig.7B) system and the E_a value was calculated as 180 kJ/mol. This concludes that ES system consumes more amount of heat energy for crosslinking of HDPE than EC system. The lower E_a value supported higher % crosslinking for EC than ES system. The % crosslinking values are listed in Table-3. Effect of temperature on C=C formation was discussed further. Fig.8A shows the plot of $1/T$ against $\log(RI_{[C=C/C-H]})$ for EC system and the E_a value was determined as 113 kJ/mol. Fig.8B shows the same type of plot for ES system and the E_a value was determined as 145 kJ/mol. Here the lower E_a value supported higher % C=C formation for EC than ES systems. The % C=C formation are shown in Table - 2.

Table 2 Effect of Temperature on functionalization, crosslinking and C=C formation

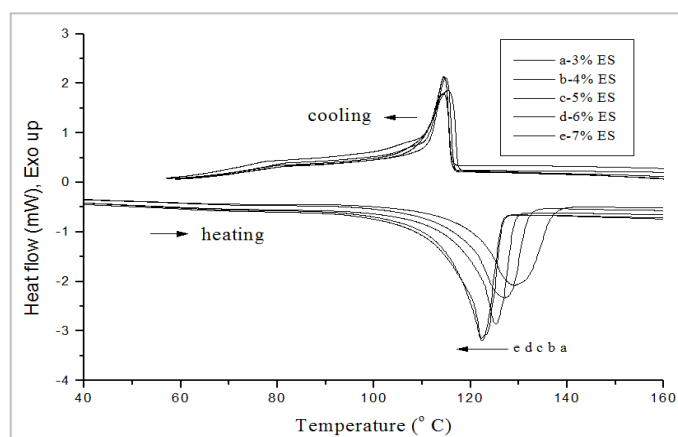
Temperature (K)	% functionalization		% crosslinking		% C=C formation	
	EC	ES	EC	ES	EC	ES
413	18.38	65.09	59.0	413	18.38	65.09
423	21.92	82.04	65.5	423	21.92	82.04
433	25.34	87.76	72.3	433	25.34	87.76
443	31.85	80.15	78.1	443	31.85	80.15
453	22.21	71.52	88.6	453	22.21	71.52

3.4. Effect of time on % functionalization, % crosslinking and C=C formation

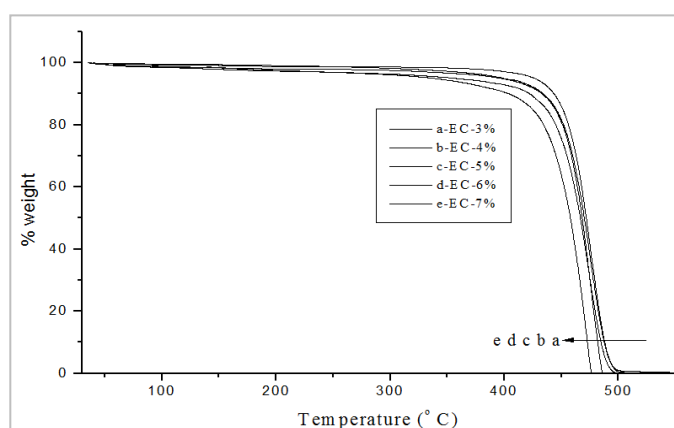
Grafting of esters onto HDPE in the presence of DCP was carried out at different intervals of time. Fig.9A represents the effect of time on % ester grafting for EC system. The plot shows a straight line and infers that increase in time leads to increase in % ester grafting i.e., increase of $RI_{[C=O/C-H]}$. Longer interval of reaction time leads to the possible interaction between HDPE macro radicals with ester radicals resulting in higher % of grafting. The same trend was noticed for the ES system too (Fig.9B). Fig.10A and Fig.10B confirmed the increase of % crosslinking with the increase of reaction time. This will allow the coupling between HDPE macro radicals. Effect of time on % of C=C double bond formation, for EC and ES system was also investigated and was shown in Fig.11A and Fig.11B respectively. Increase in the reaction time step up the % of C=C double bond formation in a linear manner. This may be due to the thermal oxidation degradation reaction. The % functionalization, crosslinking and C=C formation values are listed in Table- 3.

Table 3 Effect of Time on functionalization, crosslinking and C=C formation

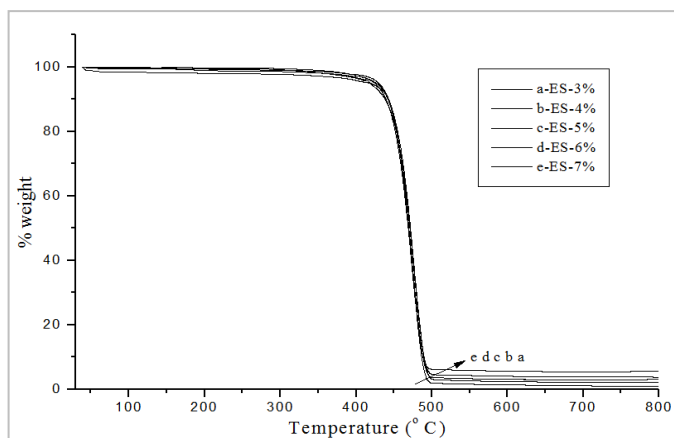
Time (sec)	% functionalization		% cross linking		% C=C formation	
	EC	ES	EC	ES	EC	ES
3600	6.61	10.46	80.0	59.5	1.95	0.51
5400	11.02	21.66	82.5	67.5	2.56	0.74
9000	23.60	23.59	88.0	72.5	3.80	1.11
10800	45.62	55.51	91.5	78.0	5.75	1.88
12600	55.87	75.41	93.0	81.5	7.62	3.08

**Figure 13**

DSC of ES functionalized HDPE at different % weight of ES

**Figure 14**

TGA of EC functionalized HDPE at different % weight of EC

**Figure 15**

TGA of ES functionalized HDPE at different % weight of ES

3.5. DSC Profiles

Melt functionalization of HDPE with different esters such as EC and ES will alter the physical and chemical properties of HDPE. The thermal behavior of functionalized HDPE can be characterized by two methods namely DSC and TGA. First the results on DSC were discussed. The % weight of EC reduced the T_m value and is shown in Fig.12. The reasons are as follows: 1) The change in the micro structure appearance of HDPE (α or β or γ form) slightly modifies during the melt functionalization process 2) It may be due to the chain scission of HDPE with terminal double bonds 3) Chain scission process leads to the decrease in molecular weight which accounts for the reduction in T_m 4) It may be due to the formation of double bond in the middle of HDPE chain. In the case of

crystallization temperature (T_c), much difference was not observed. But in the present investigation, nucleation due to grafted EC was not observed. Fig.13 shows the DSC of different % weight loading of ES functionalised HDPE system. Here also, the T_m value reduced while increasing the % weight of ES. The grafted ES side chains had not influenced T_c of HDPE. The T_c values decreased corresponding to the increase of % weight of ES. This indicates that during the melt functionalization of HDPE with ES, the crystallinity values were reduced. Further research work on GPC measurement is going on in our laboratory.

3.6. TGA history

The thermal stability of functionalised HDPE was tested with the help of TGA instrument. The TGA was recorded at the heating rate of $10^{\circ}\text{C}/\text{min}$ under air atmosphere. The TGA of EC functionalised HDPE is shown in Fig.14. The thermogram shows a single step degradation process, and upto 450°C there is no change in the structure of HDPE. The major weight loss started around 460°C and extended upto 500°C . This accounts for the scission of polymer backbone. The important point noted here is while increasing the % weight of EC the thermal stability of HDPE was slightly affected. Due to the random grafting of EC onto HDPE, the extra thermal stability due to grafted side chain was not observed. The point to be noted here is while increasing the % weight of EC the T_{id} is shifted towards lower temperature with slight decrease in degradation temperature of HDPE. Fig.15 shows the TGA of ES functionalised HDPE. There was almost no change in thermal stability due to the random functionalization of ES in the presence of DCP. Due to the random grafting of ES onto HDPE, with very low % of ES used for functionalization process, the extra thermal stability due to grafted ES was not observed. But there was no change in the thermal degradation temperature (T_d) of ES functionalized HDPE. One more interesting observation is, the % weight residue that remains above 700°C increases with the increase of % weight of ES. This concludes that even after melt functionalization with ES the thermal degradation temperature of HDPE was not affected.

4. CONCLUSION

i) The area of $\text{C}=\text{O}$ peak increases with increase in % grafting. ii) The % functionalization is higher for ES than for EC. iv) EC consumes more amount of heat energy for functionalization than for ES. v) ES consumes more amount of heat energy for crosslinking than for EC. vi) DSC concludes the decrease in T_m and T_c for both esters functionalized HDPE. vii) TGA explores the decrease in initial degradation temperature for EC-HDPE system. viii) The HDPE-ES system shows an increase in % weight residue that remains above 700°C with the increase of % weight of ES.

SUMMARY OF RESEARCH

1. Polyolefins create more environmental pollution world-wide due its non-biodegradable nature.
2. To develop biodegradable polymer, active research attempts are taken around the world for the past four decades.
3. In our study, polyethylene was functionalized with different esters in the presence of free radical initiator.
4. The Functionalized polyethylene can be biodegradable easily with the help of soil living microorganism.
5. The thermal stability of functionalized polyethylene was analyzed by TGA and DSC like analytical tools.

FUTURE ISSUES

During the functionalized process, both crosslinking and $\text{C}=\text{C}$ formation were competitive and those things should be controlled to improve the efficiency of the functionalized polymer.

Disclosure statement

DST, New Delhi is gratefully acknowledged for their financial support (Ref. No. SR/FTP/CS-39/2005).

Acknowledgments

We thank our guide for his constant support and encouragement throughout the research work.

Conflicts of interests

The authors declare that there are no conflicts of interests.

Data and materials availability

All data associated with this study are present in the paper.

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